ARB Workgroup Meeting to Discuss "Weekend Effects" Research
April 13, 2000
Presentation: Improved Detection Limits for Automated TNMOC Analyzer
By: Donald Hammond ARB/MLD

Background: The California Air Resources Board began a routine seasonal sampling program in 1989 to gather information about total non-methane organic compounds (TNMOC), principally hydrocarbons, in the high ozone areas of the state. Beginning in 1994, Federal regulations require states to establish photochemical assessment monitoring stations (PAMS) as part of their State Implementation Plan monitoring networks in ozone non-attainment areas classified as serious, severe, or extreme. The PAMS program is intended to supplement ozone monitoring and add detailed sampling for its precursors. The current ozone non-attainment areas in California subject to these requirements are: South Coast, Sacramento, San Diego, San Joaquin Valley, Santa Barbara, Mojave Desert, and Ventura. The local air pollution districts in the affected areas are full participants in the PAMS monitoring activities. For more information, visit our web site at: **http://www.arb.ca.gov/aaqm/hcarbons.htm**

The first table titled **"California PAMS Network 1999"** is a summary of our PAMS network in 1999 for hydrocarbons, carbonyls, ozone, oxides of nitrogen, and meteorology. Monitoring for hydrocarbons and carbonyls begins in June or July and continues through September. The ARB and Districts and have 16 TNMOC continuous analyzers in the field as part of the PAMS network (7^{th} column under the NMOC heading). Most of these analyzers are the Thermo Environmental Instruments Inc. (TEI) model 55 C, sometimes referred to as the "TECO 55."

The standard TECO 55 has a reported detection limit of 150 PPBC, while a modified upgrade first used by Ventura County APCD has a reported detection limit of 75 PPBC. The latter version of the analyzer is referred to as the Ventura option. The TECO 55 Ventura option samples twice as much air than the standard model. The TEI description of the TECO 55, Ventura option is provided on the page, titled **"Manual Addendum."** The linearity and detection limits of the analyzers were confirmed by MLD staff for both models with the results shown in the first two figures titled **"TECO 55 Linearity (PE&S unit),"** and **TECO 55 Linearity with Ventura modification (SD) Unit)."** Both versions of the TECO 55 can only accept a one-point calibration using propane (in these examples at 1500 PPBC); however, at the lower concentrations, as shown in the figures, the TECO 55 will report lower than expected values. The TECO 55 with the Ventura modification clearly performed better than the standard version but are currently only deployed in Ventura County. During the summer of 1999, much of the reported TNMOC data from the standard TECO 55s were reported below the LOD (150 PPBC). The Districts and ARB/MLD have decided to send all standard TECO 55's in the PAMS program back to TEI for an upgrade to the Ventura modification. The improved analyzers should be in place by the beginning of this summer.

A comparison of three different methods used to measure TNMOC in the PAMS program are compared at stations where all the results are above the method detection limits. Canisters sampled for three hours, four times a day are analyzed in the laboratory for 55 specific hydrocarbons. The sum of these hydrocarbons plus others quantified but not identified in the sample is reported to AIRS as TNMOC method 200. A second laboratory analysis of the same canister sample is performed on the non-separated organic compounds and reported as TNMOC method 200.

An evaluation of the three methods is hindered by the limited number of results from the TECO 55 that were above the 150 PPBC detection limits. Over a two-summer period (1998 and 1999) four stations during the morning canister-sampling period were found to have a sufficient number of matched points to generate a trend graph. **Four trend figures were presented**. In general, all the methods followed the same pattern. Method 164 (TECO 55 standard version) was generally higher in concentration than the canister collected methods. Once the relationship among the different TNMOC methods are better established the TECO 55 can provide the data users addition hydrocarbon information during days when the canister samples are not taken. The deployment of the analyzers with the Ventura modification will result in the better collection of TNMOC measurements at the lower levels found in ambient air.

California PAMS Network 1999

Station	AIRS #	O3	NOx	CSGC	HCS	NMOC	MTGC	C=O	UA	W	T	RH	SR	UV	BP	R	V
Ventura County APCD																	
Simi Valley- Cochran #3	061112002	X	X		X	X				X	X	X	X	X			
El Rio #2	061113001	X	X		Xparallel	X		X-split		X	X	X	X				
Ventura- Emma Wood #1	061112003	X	X		X	X				X	X	X	X				
Simi Valley- landfill	061110008								X	X	X	X	X		X	X	X
Santa Barbara APCD																	
Goleta #2- CSGC nearby office	06832011	X	X	New!				New!		X	X						
Santa Barbara Airport New!	none								X	X	X	X	X		X		
San Diego APCD																	
El Cajon #2	060730003	X	X		X	X		X-split		X	X	X					
S.D. Overland #2	060730006	X	X		X			X-split		X	X	X			X		
Alpine #3	060731006	X	X		X					X	X	X					
Camp Pendleton #1	060731008	X	X		X					X	X						
Point Loma / Miramar New!	none								X	X	X						
Sacramento M-AQMD																	
Sac- Del Paso Manor #2	060670006	X	X		X	X	X	X		X	X	X	X				
Folsom-50 Natoma #3	060670012	X	X		X	X	X			X	X	X	X				
Elk Grove- Bruceville #1	060670011	X	X		X	X	X		X	X	X	X	X	X	X	X	
Sac- Airport Rd. #2	060670013	X	X		X	X	X	X		X	X	X	X				
San Joaquin VU-APCD																	
Bakersfield- Golden #2 (ARB)	060290010	X	X		X	X	X	X		X	X	X	X		X		
Fresno- Clovis #2	060195001	X	X		X	X	X	X		X	X	X	X		X		
Arvin #3 / #1 (ARB)	060295001	X	X		X	X	X			X	X	X	X		X		
Parlier # 3	060194001	X	X		X	X	X			X	X	X	X		X		
Madera #1	060390004	X	X		X	X	X			X	X	X	X		X		
Shafter #1 (ARB)	060296001	X	X		X	X	X			X	X	X	X		X		
Visalia-airport	061073000								X	X	X	X	X		X		
South Coast AQMD																	
Pico Rivera #2	060371601	X	X	X				X-split		X	X	X	X	X	X		
Azusa #3	060370002	X	X		X					X	X	X	X	X	X		X
Banning-Airport #2	060650012	X	X		X			X		X	X	X	X	X	X		
Upland #4 / #1	060711004	X	X		X					X	X	X	X	X	X		
Hawthorne #1	060375001	X	X		X					X	X	X	X	X	X		
Burbank #2	060371002	X	X	X				X		X	X	X	X	X	X		
Santa Clarita #2 New!	06037????	X	X		X			X		X	X	X	X	X	X		
LAX / Ontario X	none								X	X	X	X	X	X	X		
PAMS Value Added Sites																	
Fresno- 1st (ARB)	060190008	X	X		X-colloc.	X	X-colloc.	X-split		X	X						
LA- North Main	060371103	X	X		X		X			X	X	X	X	X			
San Diego- 12th	060731007	X	X		X	X	X			X	X						

New! – New station for 1999
O3- Ozone
NOx- Oxides of Nitrogen
CSGC- Continuous 3 hour Speciated hydrocarbon Gas Chromatography
HCS- HC Species by canister GC
NMOC- Total Non-Methane Organic Compounds, continuous, hourly monitoring
RH- Relative Humidity
MTGC- Measured TNMOC, GC, canister, (PDFID)
C=O- Carbonyls, 3 hour cartridges
UA- Upper Air monitoring
W- Wind speed /direction
T- Temperature, ambient
SR- Solar Radiation, total
UV- UltraViolet radiation
BP- Barometric Pressure
R- Rain
V- Visibility

arb/mld/pe&s/dsh/4-12-99

Source: Bob Mouradain, TEI 4-11-0

Manual Addendum
Model 55C - Ventura Option

Introduction:

The Model 55C Ventura option provides an improved limit of detection (LOD) for non-methane measurements. The improved LOD is achieved through increased sample size, column modifications that reduce the time to back-flush, re-optimization of gas flows, and enhancement of the integration algorithms. As a result of these changes, the LOD for non-methane hydrocarbons is reduced to approximately 75 ppbc and the instrument cycle time is reduced to between 55 and 60 seconds. In this case, LOD is defined as the concentration that produces a peak height equal to the average base line signal plus three times the standard deviation of the noise. As a practical matter, this is the lowest concentration that can be reliably detected as a non-zero reading. And, when replicate measurements of a test gas are taken at approximately 75 ppbc, the coefficient of variation is expected to be 10% or better.

While these design changes improve overall performance for measurement of non-methane hydrocarbons, the large sample volume prevents separation of methane from oxygen. Due to the overlap of the methane and oxygen peaks, the methane channel cannot be accurately "zeroed" on span gas, as is done in the standard 55C. Therefore, the accuracy, precision, and LOD for methane measurements may not match the performance seen with the standard design. To help compensate for this, a zero subtraction, or offset, capability has been added to the instrument software. With the zero subtraction activated, the calibration routine is enhanced so that a zero-air chromatogram can be run along with the normal span gas chromatogram. The zero-air baseline will then be subtracted from subsequent measurement cycles, which will improve measurement accuracy at low methane concentrations.

Hardware and Timing Modifications:

1. Sample Loop: A 2 cc sample loop has been installed.

2. Chromatography Column: The standard column has been replaced with modified Ventura column.

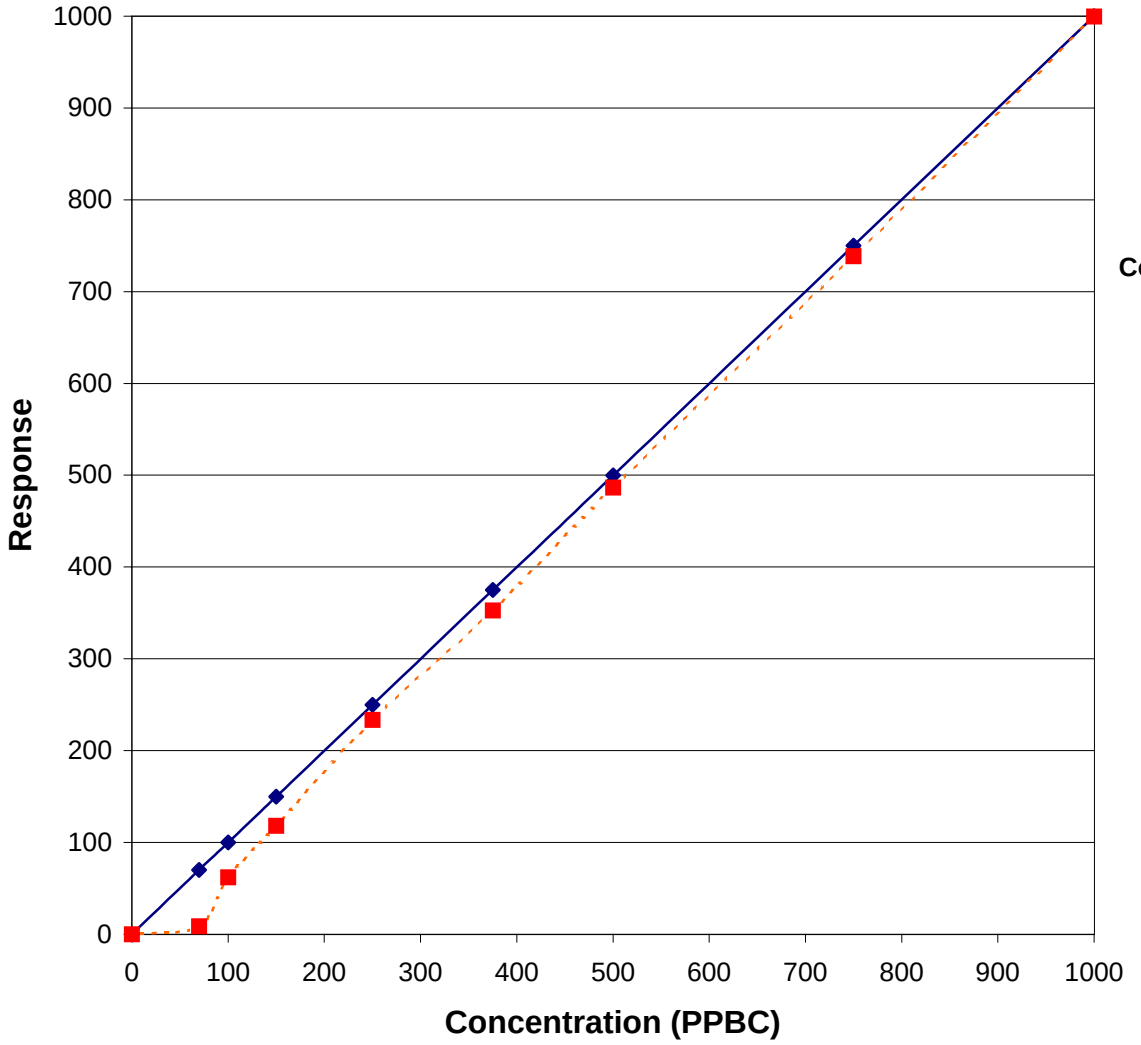
3. Carrier Flow Restrictor: The standard flow restrictor has been replaced with a modified version that is matched to the new column.

4. Software: The standard EEPROM has been replaced with software version.

5. Carrier Adjustment: The carrier gas pressure has been adjusted to reduce the methane retention time to between 10 and 12 seconds compared to the standard 17 seconds.

6. Window Timing: The methane window, back-flush time and nonmethane window have been adjusted as required for the shorter retention time.

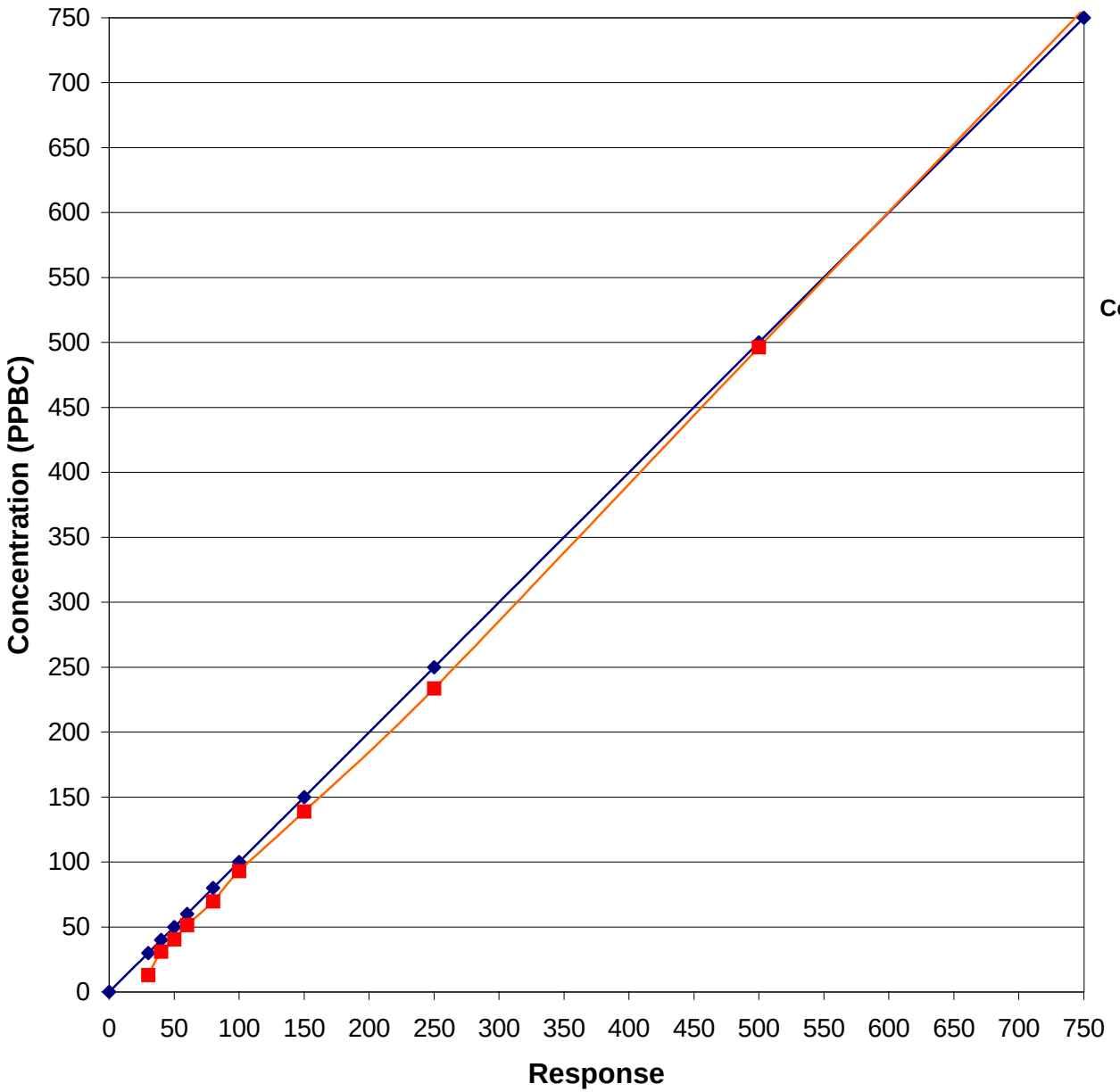
TECO 55 Linearity (PE&S unit)

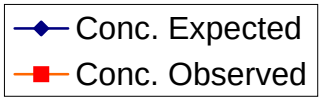


Conc. Expected	Conc. Observed	% Difference
1500	1494	0
1000	1000	0
750	738	-2
500	486	-3
375	353	-6
250	234	-7
150	118	-21
100	62	-38
70	9	-88
0	0	0

dsh/pe&s/1-14-0

TECO 55 Linearity with Ventura modification (SD Unit)





Conc. Expected	Conc. Observed	% Difference
750	757	1
500	496	-1
250	234	-7
150	139	-7
100	93	-7
80	70	-13
60	52	-14
50	41	-19
40	31	-23
30	13	-57
0		

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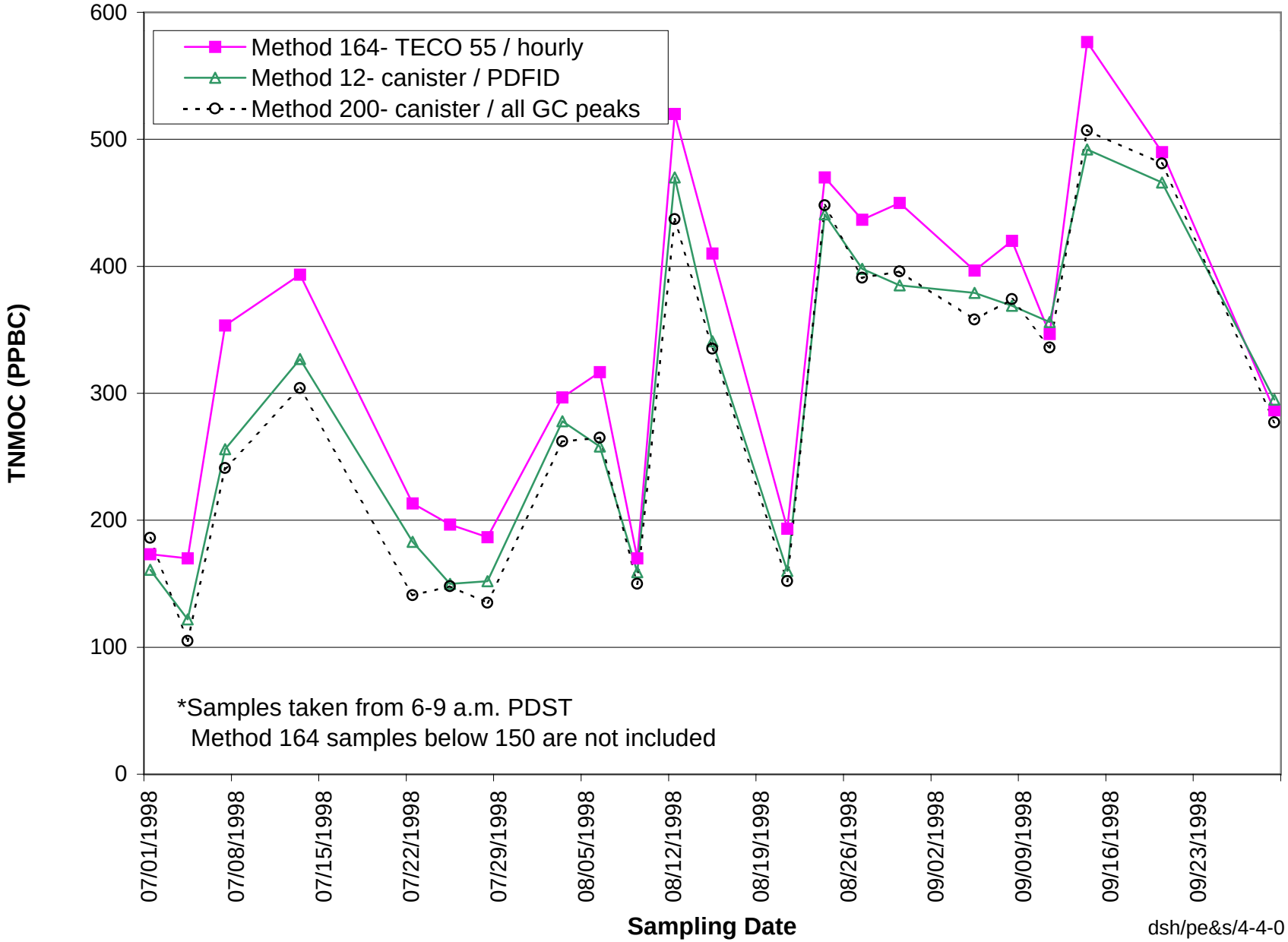
TNMOC at Fresno 1st for 1998 - Methods 164, 12, and 200*



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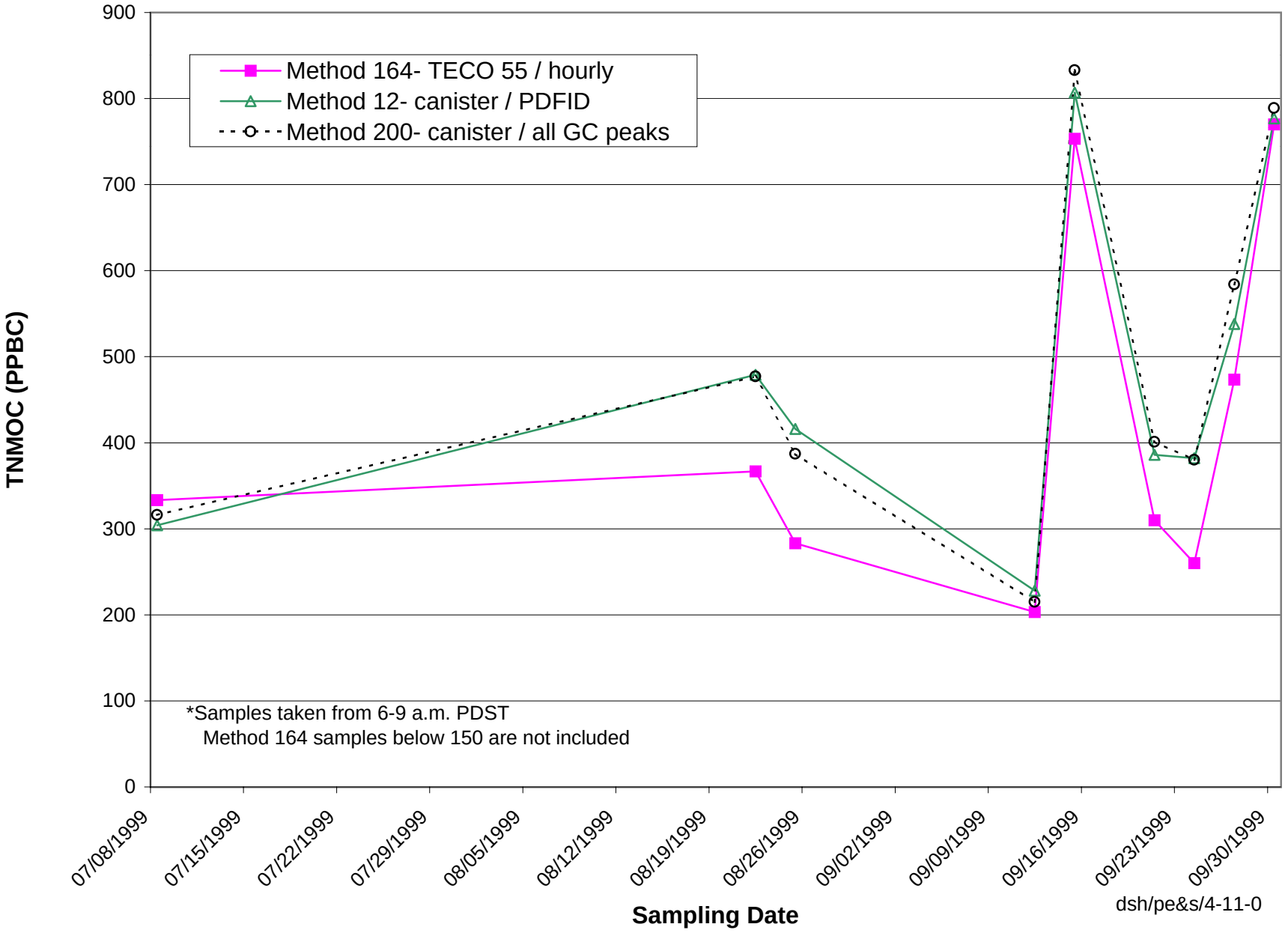
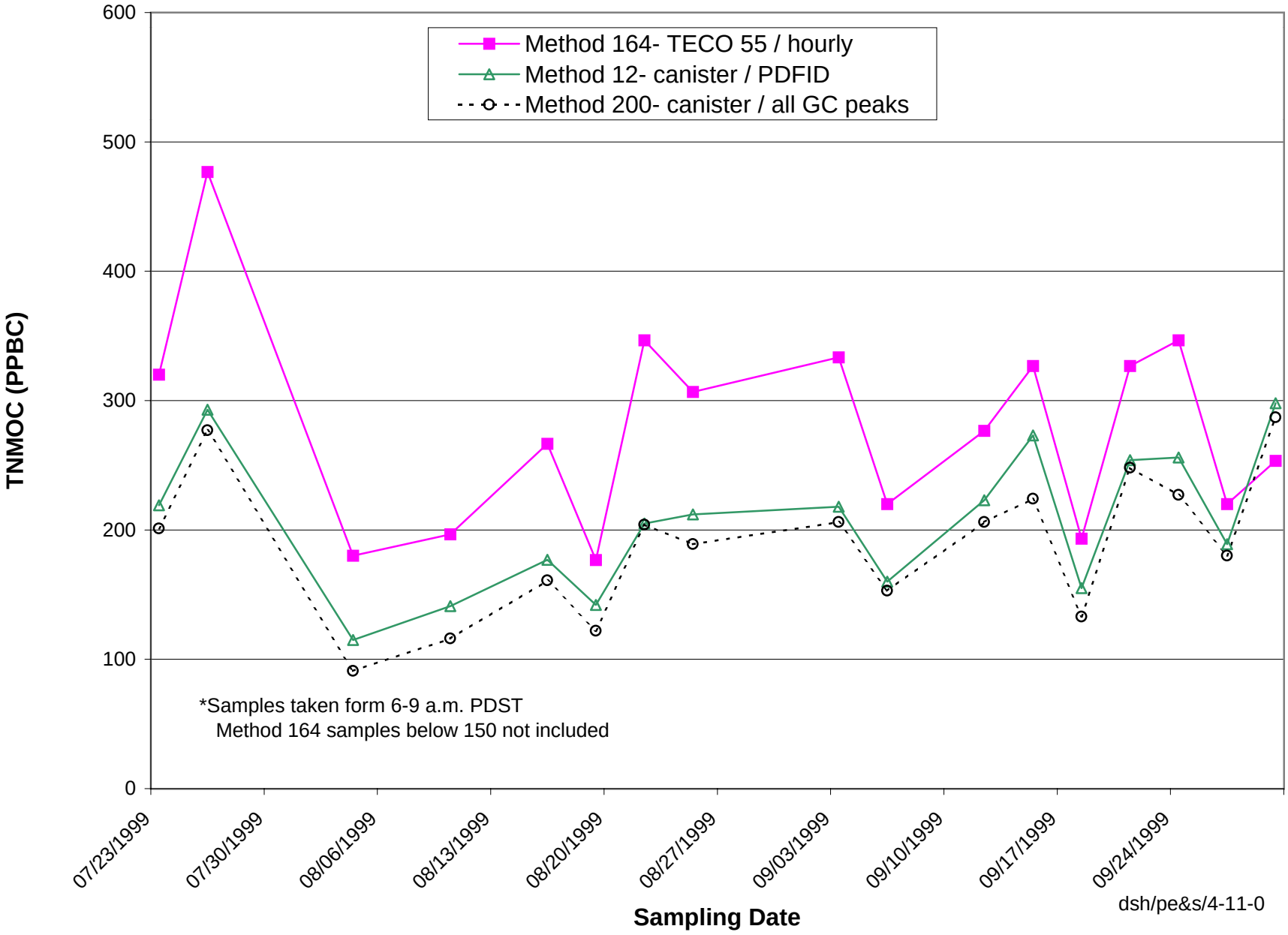
TNMOC at Fresno 1st for 1999 - Methods 164, 12, and 200*



TNMOC at Parlier for 1999 - Methods 164, 12, and 200*



TNMOC at Shafter for 1999 - Methods 164, 12, and 200*